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**Multidimensional Thermochemical Cycles – Exploring Three Dimensions:  
Designer Tool for Estimation of the Thermodynamics of Reactions at Varying  
Conditions and for Estimating Elusive Thermodynamic Data**

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*This paper is dedicated to Professor Manuel Ribeiro da Silva, late of the Universidade do Porto, Portugal – a distinguished thermochemist and esteemed colleague.*

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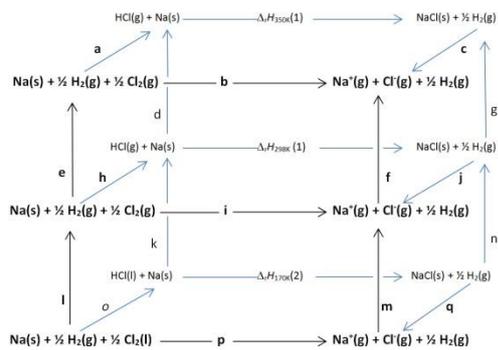
## **Abstract**

Born-Haber-Fajans (BHF) thermochemical cycles describe links among different aspects of a chemical reaction at a common temperature and pressure, independent of the actual process of the reaction, and so provide methods for evaluation of otherwise missing information. We show that the standard two-dimensional BHF cycle can be extended to allow for consideration of temperature and pressure variation, here using temperature changes for the reaction between HCl and Na as our illustrative example. Such extension provides possibilities of multiple interrelationships among contemplated states of the process of the reaction, so enhancing the related thermodynamic information. Although thermodynamics and kinetics do not necessarily coincide, it may be possible, utilizing such insights, to circumvent kinetically-disallowed steps in a chemical synthesis by choosing an alternative but thermodynamically favoured route.

## **Keywords**

Thermochemical Cycle; Born-Haber-Fajans; Thermodynamic Relations

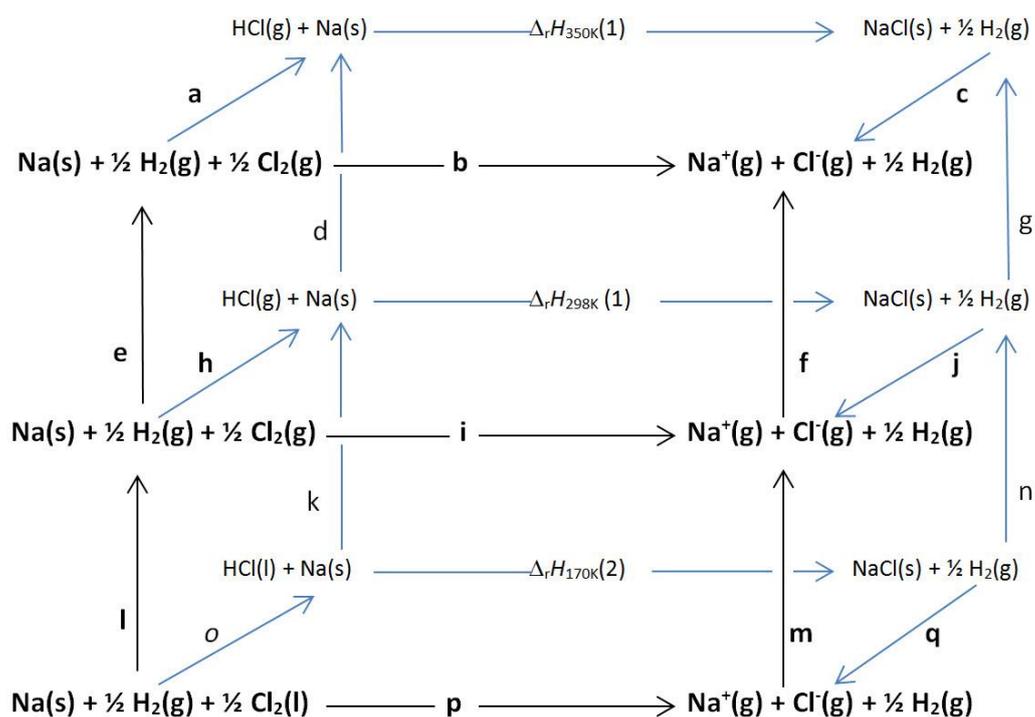
# Graphical Abstract



## 1. Introduction

Most chemists are familiar with two-dimensional Born-Haber-Fajans cycles, which provide alternative routes by which the thermochemistry of the various key thermodynamic parameters ( $\Delta_r H$ ,  $\Delta_r S$ ,  $\Delta_r G$ ,  $U_{\text{POT}}$  - where  $U_{\text{POT}}$  is the lattice potential energy) may be evaluated at fixed temperature and pressure, when the direct route may not be accessible. This is possible because these parameters are state functions,[1] independent of the history of the system considered.

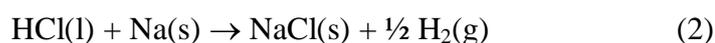
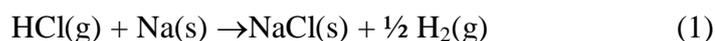
However, the standard limitation to two dimensions may readily be extended to multiple dimensions[2] by including variation in both temperature and pressure, which provides opportunities for deeper exploration of the interrelations of the thermodynamic parameters. We limit ourselves here to *three* dimensions in illustrating the concept, our purpose in this paper being to point out that, once constructed, such a cycle offers a ready means of identifying multiple possible routes (and hence key interrelationships) between any given set of reactants and products and thereby a means of acquiring new thermodynamic data within the framework of a simple graphical concept. This is in accord with increasing current practice in synthetic inorganic chemistry of including thermodynamic data and relating this data to other similar materials.



**Figure 1:[2]** Three-Dimensional Thermochemical Cycle based on reactions at 350K, 298K and 170K between HCl and Na, leading to the products NaCl and hydrogen gas (horizontal rear edges), the formation reactions at 350K, 298K and 170K of the reactants (horizontal left-hand side edges: a, h, o), the lattice potential energies at 350K, 298K and 170K (horizontal right-hand side edges: -c, -j, -q), the formation reactions at 350K, 298K and 170K of the gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions (horizontal front edges: b, i, p). Vertical edges d, e, f, g, k, l, m, n involve heat capacity terms required to raise the temperature of elements in their standard states (vertical, front, left hand side: e, l), gaseous ions and  $\text{H}_2(\text{g})$  (vertical, front, right-hand side: f, m), products (vertical, rear, right-hand side: g, n) and reactants (vertical, rear, left-hand side: d, k). Note the following:[3]  $\text{HCl}(\text{g})$  condenses to become  $\text{HCl}(\text{l})$  at 188K, while  $\text{Cl}_2(\text{g})$  condenses to become  $\text{Cl}_2(\text{l})$  at 239K.

## 2. Three Dimensional Representations

Consider, for example, Figure 1 in which two specific reactions are considered at three temperatures, 170K, 298K and 350K, chosen to cover both the liquid and gaseous states of hydrochloric acid and chlorine, all at ambient pressure:



There are, needless to say, many other processes which can involve Na, H and Cl.

Since the enthalpy change for reaction (1) is a thermodynamic function of state, it is of course independent of the route taken between reactants and products. Thus, a whole series of thermodynamic relationships (eq. 3 – 15 below) can be written, any one of which will enable the calculation of  $\Delta_r H_{350\text{K}}(1)$ . It should be noted that these individual relations may not necessarily be straight-forward, and may themselves require to be evaluated by means of independent Born-Haber-Fajans cycles (cf. Supplementary Information).

A number of thermodynamic parameters involved in the cycle have not been evaluated; these, *inter alia*, include:  $[\Delta_f H_{350\text{K}}(\text{Na}^+, \text{g}) + \Delta_f H_{350\text{K}}(\text{Cl}^-, \text{g})]$ ,  $\Delta_r H_{170\text{K}}(2)$ ,  $\Delta_{\text{vap}} H^\circ(\text{HCl, l})$ ,  $\Delta_f H_{170\text{K}}(\text{HCl, l})$  and  $[\Delta_f H_{170\text{K}}(\text{Na}^+, \text{g}) + \Delta_f H_{170\text{K}}(\text{Cl}^-, \text{g})]$ .

### 2.1 Cycle Relationships

Using the various routes possible between reactants and products we can write:

$$\Delta_r H_{350\text{K}}(1) = -a + b - c \quad (3)$$

$$\Delta_r H_{350\text{K}}(1) = -d + \Delta_r H_{298\text{K}}(1) + g \quad (4)$$

$$\Delta_r H_{350\text{K}}(1) = -a - e + h + \Delta_r H_{298\text{K}}(1) + g \quad (5)$$

$$\Delta_r H_{350\text{K}}(1) = -a - e + i - j + g \quad (6)$$

$$\Delta_r H_{350\text{K}}(1) = -a - e - l + p - q + n + g \quad (7)$$

$$\Delta_r H_{350\text{K}}(1) = d - k + \Delta_r H_{170\text{K}}(2) + n + g \quad (8)$$

$$\Delta_r H_{350\text{K}}(1) = -a + b - f - m - q + n + g \quad (9)$$

$$\Delta_r H_{350\text{K}}(1) = -a + b - f - j + g \quad (10)$$

$$\Delta_r H_{350\text{K}}(1) = -a - e + i - f - c \quad (11)$$

$$\Delta_r H_{350\text{K}}(1) = -a - e - l + o + K + \Delta_r H_{298\text{K}}(1) + g \quad (12)$$

$$\Delta_r H_{350\text{K}}(1) = -a - e - l + o + \Delta_r H_{170\text{K}}(2) + n + g \quad (13)$$

$$\Delta_r H_{350\text{K}}(1) = -d - h - l + p - q + n + g \quad (14)$$

$$\Delta_r H_{350\text{K}}(1) = -d - h + i - j + g \quad (15)$$

The individual edges can be linked to thermodynamic data as follows, with  $C_p$  in units of  $\text{J K}^{-1} \text{mol}^{-1}$ :

$$a = \Delta_f H_{350\text{K}}(\text{HCl}, \text{g}) / (\text{kJ mol}^{-1}) = -92.4 \quad (16)$$

$$b = \Delta_f H_{350\text{K}}(\text{Na}^+, \text{g}) + \Delta_f H_{350\text{K}}(\text{Cl}^-, \text{g}) \quad (17)$$

$$c = [U_{\text{POT}}(\text{NaCl}) - RT] / (\text{kJ mol}^{-1}) = U_{\text{POT}}(\text{NaCl}) - 2.91 \quad (18)$$

$$d = [C_p(\text{HCl}, \text{g}) + C_p(\text{Na}, \text{s})] \Delta T \quad (19)$$

$$e = [\frac{1}{2}C_p(\text{H}_2, \text{g}) + \frac{1}{2}C_p(\text{Cl}_2, \text{g}) + C_p(\text{Na}, \text{s})] \Delta T \quad (20)$$

$$f = [C_p(\text{Na}^+, \text{g}) + C_p(\text{Cl}^-, \text{g}) + \frac{1}{2}C_p(\text{H}_2, \text{g})] \Delta T \quad (21)$$

$$g = [C_p(\text{NaCl}, \text{s}) + \frac{1}{2}C_p(\text{H}_2, \text{g})] \Delta T \quad (22)$$

$$h = \Delta_f H^0(\text{HCl}, \text{g}) \quad (23)$$

$$i = [\Delta_f H^0(\text{Na}^+, \text{g}) + \Delta_f H^0(\text{Cl}^-, \text{g})] \quad (24)$$

$$j = [U_{\text{POT}}(\text{NaCl}) - RT]/(\text{kJ mol}^{-1}) = U_{\text{POT}}(\text{NaCl}) - 2.48 \quad (25)$$

$$k = C_p(\text{HCl}, \text{l})\Delta T' + \Delta_{\text{vap}} H^0(\text{HCl}, \text{l}) + C_p(\text{HCl}, \text{g}) \Delta T'' + C_p(\text{Na}, \text{s}) \Delta T''' \quad (26)$$

$$l = [\frac{1}{2}C_p(\text{H}_2, \text{g}) \Delta T'''' + \frac{1}{2}C_p(\text{Cl}_2, \text{l}) \Delta T'''' + \Delta_{\text{vap}} H^0(\text{Cl}_2, \text{l}) + \frac{1}{2}C_p(\text{Cl}_2, \text{g}) \Delta T'''' \quad (27)$$

$$m = [C_p(\text{Na}^+, \text{g}) + C_p(\text{Cl}^-, \text{g}) + \frac{1}{2}C_p(\text{H}_2, \text{g})] \Delta T'''' \quad (28)$$

$$n = [C_p(\text{NaCl}, \text{c}) + \frac{1}{2}C_p(\text{H}_2, \text{g})] \Delta T'''' \quad (29)$$

where the various temperature differences,  $\Delta T$ , refer to the intervals between phase changes of HCl and of Cl<sub>2</sub>.

$$o = \Delta_f H_{170\text{K}}(\text{HCl}, \text{l}) \quad (30)$$

$$p = [\Delta_f H_{170\text{K}}(\text{Na}^+, \text{g}) + \Delta_f H_{170\text{K}}(\text{Cl}^-)] \quad (31)$$

$$q = [U_{\text{POT}}(\text{NaCl}) - RT] / \text{kJ mol}^{-1} = U_{\text{POT}}(\text{NaCl}) - 1.45 \quad (32)$$

### 3. Quantitative Evaluation of Unknown Thermochemical Data

#### 3.1 $\Delta_r H_{350\text{K}}(1)/\text{kJ mol}^{-1}$

Equations (6), (11) and (15) provide direct estimates for  $\Delta_r H_{350\text{K}}(1)$  of  $-314.3 \text{ kJ mol}^{-1}$ ,  $-314.8 \text{ kJ mol}^{-1}$  and  $-314.0 \text{ kJ mol}^{-1}$  respectively, averaging to:

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = -314.4 \quad (33)$$

### 3.1.1 Edge *b*

Adopting the value above for  $\Delta_r H_{350\text{K}}(1)$ , we can evaluate *b* from equations (3), (9) and (10) to be 376.6 kJ mol<sup>-1</sup>, 378.5 kJ mol<sup>-1</sup> and 375.9 kJ mol<sup>-1</sup>, respectively, averaging to:

$$b/(\text{kJ mol}^{-1}) = 376.9 \quad (34)$$

### 3.1.2 $\Delta_r H_{298\text{K}}(1)/(\text{kJ mol}^{-1})$

Adopting the value above for  $\Delta_r H_{350\text{K}}(1)$ , equations (4) and (5) provide direct estimates of -314.8 kJ mol<sup>-1</sup> and -314.5 kJ mol<sup>-1</sup>, respectively, averaging to:

$$\Delta_r H_{298\text{K}}(1)/(\text{kJ mol}^{-1}) = -314.6 \quad (35)$$

The remaining equations (7), (8), (12), (13) and (14) take the form:

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = p - l - 683 \quad (36)$$

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = 10 - k + \Delta_r H_{170\text{K}}(2) \quad (37)$$

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = 92.3 - l + o + k + \Delta_r H_{170\text{K}}(2) \quad (38)$$

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = 102.2 - l + o + \Delta_r H_{170\text{K}}(2) \quad (39)$$

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = -682.7 - l + p \quad (40)$$

### 3.1.3 Edge *k*

Subtracting equation (38) from (39) leads to:

$$k/(\text{kJ mol}^{-1}) = 9.8 \quad (41)$$

representing the enthalpy involved in a change of state of HCl from liquid to gas as its temperature is raised from 170K to 298K in the presence of solid sodium (without any reaction taking place between them) which suffers a similar rise in temperature.

$$\Delta_r H_{170\text{K}}(2)$$

From the value for  $k$  above, equation (37), and the above results:

$$\Delta_r H_{170\text{K}}(2)/(\text{kJ mol}^{-1}) = -314.6 \quad (42)$$

#### 4. Quantification of Enthalpy changes for complex reactions

##### 4.1 Thermodynamics Associated with Edges $o$ , $p$ and $l$

Using equations (36) and (40) leads to:

$$(p - l)/(\text{kJ mol}^{-1}) = 368.4 \quad (43)$$

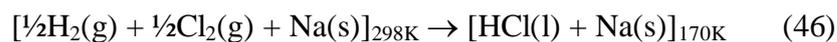
and this enthalpy change corresponds to that for the process:



Averaging values after substituting in equations (38) and (39) leads to:

$$(o - l)/(\text{kJ mol}^{-1}) = -101.9 \quad (45)$$

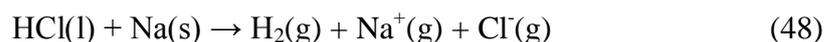
which corresponds to the enthalpy change for the reaction:



Using equations (39) and (40) leads to:

$$(p - o)/(\text{kJ mol}^{-1}) = 470.3 \quad (47)$$

which corresponds to the enthalpy change for the following reaction at 170K:



### 5. Confirmatory Data

By way of confirmatory data, in addition we can estimate  $\Delta_r H_{350\text{K}}(1)$  from the following direct thermodynamic relationships.

$$\Delta_r H_{350\text{K}}(1) = \Delta_f H_{350\text{K}}(\text{NaCl, s}) + \frac{1}{2} \Delta_f H_{350\text{K}}(\text{H}_2, \text{g}) - \Delta_f H_{350\text{K}}(\text{HCl, g}) - \Delta_f H_{350\text{K}}(\text{Na, s}) \quad (49)$$

Taking  $\Delta_f H_{350\text{K}}(\text{NaCl, s})/(\text{kJ mol}^{-1}) = -412.2$  [4] and  $\Delta_f H_{350\text{K}}(\text{HCl, g})/(\text{kJ mol}^{-1}) = -92.4$ . The data used are average values and lead to:

$$\Delta_r H_{350\text{K}}(1)/(\text{kJ mol}^{-1}) = -319.7 \quad (50)$$

differing by only 1.7 % from our estimate in equation (33).

Using standard state data,[4; 5]  $\Delta_f H^0(\text{NaCl, s})/(\text{kJ mol}^{-1}) = -411.1$  and  $\Delta_f H^0(\text{HCl, g})/(\text{kJ mol}^{-1}) = -92.3$

$$\Delta_r H_{298\text{K}}(1) = \Delta_f H^0(\text{NaCl, s}) + \frac{1}{2} \Delta_f H^0(\text{H}_2, \text{g}) - \Delta_f H^0(\text{HCl, g}) - \Delta_f H^0(\text{Na, s}) \quad (51)$$

$$\Delta_r H_{298\text{K}}(1)/(\text{kJ mol}^{-1}) = -318.8 \quad (52)$$

differing by only 1.3 % from our estimate in equation (35).

## 6. Conclusions

- Resorting to multi-dimensional cycles targeted towards the determination of unknown thermodynamic quantities introduces multiple relationships which enable evaluation.
- Thermodynamics for the more complex reactions represented by the diagonals of the cubes in Figure 1 can also be evaluated.
- This paper shows that “designer” cycles could be conceived to target the evaluation of the thermodynamics of a specifically targeted reaction.
- Similar cycles could be devised involving pressure changes, entropy changes,  $\Delta S$ , or Gibbs energy changes,  $\Delta G$ .
- By utilizing such insights, it may be possible to circumvent kinetically-disallowed steps in a chemical synthesis.

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## **Supplementary Material**

### **Multidimensional Thermochemical Cycles – Exploring Three Dimensions: Designer Tool for Estimation of the Thermodynamics of Reactions at Varying Conditions and for Estimating Elusive Thermodynamic Data**

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## Details of Calculations

The individual edges in Figure 1 can be linked to thermodynamic data and evaluated as follows:

$$a/(\text{kJ mol}^{-1}) = \Delta_f H_{350 \text{ K}}(\text{HCl}, \text{g}) = -92.4 \quad [1] \quad (\text{S1})$$

$$b/(\text{kJ mol}^{-1}) = \Delta_f H_{350 \text{ K}}(\text{Na}^+, \text{g}) + \Delta_f H_{350 \text{ K}}(\text{Cl}^-, \text{g}) \quad (\text{S2})$$

The data for  $b$  is not available in the literature. The lattice potential energy[2] for NaCl is found to be  $786 \text{ kJ mol}^{-1}$  at 298 K and using the fact that there is a very small variation of lattice potential energy with temperature we adopt this value throughout. Thus, correcting for the difference between energy and enthalpy:

$$c/(\text{kJ mol}^{-1}) = [U_{\text{POT}}(\text{NaCl}) - RT] = 786 - 2.91 = 783 \quad (\text{S3})$$

$$d/(\text{kJ mol}^{-1}) = [C_p(\text{HCl}, \text{g}) + C_p(\text{Na}, \text{s})]\Delta T/(\text{kJ mol}^{-1})$$

$$\approx [29.1 + \frac{1}{2}(30.1 + 28.2)](350 - 298)/1000$$

$$= [58.25](52)/1000 = 3.0 \quad (\text{S4})$$

the  $C_p(\text{Na}, \text{s})$  figure adopted being the average of the 298 K and 350 K values.[1]

$$e/(\text{kJ mol}^{-1}) = [\frac{1}{2}C_p(\text{H}_2, \text{g}) + \frac{1}{2}C_p(\text{Cl}_2, \text{g}) + C_p(\text{Na}, \text{s})]\Delta T$$

$$\approx [\frac{1}{2}\{\frac{1}{2}(29.1 + 28.8)\} + \frac{1}{2}\{\frac{1}{2}(34.7 + 33.9)\} + \frac{1}{2}(30.1 + 28.2)](350 - 298)/1000$$

$$\approx [14.48 + 17.17 + 29.15](52)/1000 = 3.2 \quad (\text{S5})$$

the  $C_p(\text{H}_2, \text{g})$ ,  $C_p(\text{Cl}_2, \text{g})$  and  $C_p(\text{Na}, \text{s})$  values being taken to be the average of the 350 K and 298 K values.[1]

$$f/(\text{kJ mol}^{-1}) = [C_p(\text{Na}^+, \text{g}) + C_p(\text{Cl}^-, \text{g}) + \frac{1}{2}C_p(\text{H}_2, \text{g})]\Delta T$$

$$\begin{aligned} &\approx [20.8 + 20.8 + \frac{1}{2}\{29.1 + 28.8\}] (350 - 298)/1000 \\ &= [56.05](52)/1000 = 2.9 \end{aligned} \quad (S6)$$

the  $C_p(\text{H}_2, \text{g})$  value being the average of the 350 K and 298 K values.[1]

$$\begin{aligned} g/(\text{kJ mol}^{-1}) &= [C_p(\text{NaCl}, \text{s}) + \frac{1}{2} C_p(\text{H}_2, \text{g})] \Delta T \\ &\approx [50.50 + \frac{1}{2}\{29.1 + 28.8\}] (350 - 298)/1000 = [64.98](52)/1000 = 3.4 \end{aligned} \quad (S7)$$

the  $C_p(\text{H}_2, \text{g})$  value being the average of the 350 K and 298 K values.[1] In the absence of a value at 350 K the 298 K value is taken for  $C_p(\text{NaCl}, \text{s})$

$$h/(\text{kJ mol}^{-1}) = \Delta_f H^\circ(\text{HCl}, \text{g}) = -92.3 \quad [3] \quad (S8)$$

$$i/(\text{kJ mol}^{-1}) = [\Delta_f H^\circ(\text{Na}^+, \text{g}) + \Delta_f H^\circ(\text{Cl}^-, \text{g})] = 609.38 - 233.13 = 376.3 \quad (S9)$$

$$j/(\text{kJ mol}^{-1}) = [U_{\text{POT}}(\text{NaCl}) - RT] = 786 - 2.5 = 783 \quad (S10)$$

$$\begin{aligned} k/(\text{kJ mol}^{-1}) &= C_p(\text{HCl}, \text{l}) \Delta T' + \Delta_{\text{vap}} H^\circ(\text{HCl}, \text{l}) + C_p(\text{HCl}, \text{g}) \Delta T'' + C_p(\text{Na}, \text{s}) \Delta T''' \\ &\approx C_p(\text{HCl}, \text{l})(188-170)/1000 + \Delta_{\text{vap}} H^\circ(\text{HCl}, \text{l}) + 29.1(298-188)/1000 + \\ &\quad \frac{1}{2}(28.2 + \frac{1}{2}\{26.0 + 22.5\})(298-170)/1000 \\ &= 0.018 C_p(\text{HCl}, \text{l}) + \Delta_{\text{vap}} H^\circ(\text{HCl}, \text{l}) + 7.08 = 0.018 C_p(\text{HCl}, \text{l}) + 16.9 + 3.36 \end{aligned} \quad (S11)$$

No data is known for  $C_p(\text{HCl}, \text{l})$ . HCl boils at 188 K at 1 atm.  $C_p(\text{HCl}, \text{g})$  has a roughly constant value[1] between 100 K and 298 K and  $C_p(\text{Na}, \text{s})$  is calculated as the average of the 298 K value and the average of the 100 K and 200 K data and:

$$\Delta_{\text{vap}} H^\circ(\text{HCl}, \text{l})/(\text{kJ mol}^{-1}) \approx 90T_b = 16.9 \quad (\text{Trouton's Rule}). \quad (S12)$$

$$\begin{aligned} l/(\text{kJ mol}^{-1}) &= \frac{1}{2}[C_p(\text{H}_2, \text{g}) \Delta T'''' + C_p(\text{Cl}_2, \text{l}) \Delta T'''' + \Delta_{\text{vap}} H^\circ(\text{Cl}_2, \text{l}) + C_p(\text{Cl}_2, \text{g}) \Delta T''''] \\ &\approx \frac{1}{2} [\frac{1}{2} (28.8 + \frac{1}{2}\{27.4 + 28.2\})(298-170) + C_p(\text{Cl}_2, \text{l})(240-170)] \end{aligned}$$

$$\begin{aligned}
& + \Delta_{\text{vap}}H^{\circ}(\text{Cl}_2, \text{l}) + \frac{1}{2} (33.9 + 31.7)(298-240)]/1000 \\
& = \frac{1}{2} [(28.3)(128) + 70 C_p(\text{Cl}_2, \text{l}) + \Delta_{\text{vap}}H(\text{Cl}_2, \text{l}) + (32.8)(58)]/1000 \\
& = \frac{1}{2} [3622 + 70 C_p(\text{Cl}_2, \text{l}) + \Delta_{\text{vap}}H(\text{Cl}_2, \text{l}) + 1902]/1000 \\
& = \frac{1}{2} [3.6 + 0.070 C_p(\text{Cl}_2, \text{l}) + 20.41 + 1.9] \\
& = 13.0 + 0.035 C_p(\text{Cl}_2, \text{l}) \tag{S13}
\end{aligned}$$

$C_p(\text{H}_2, \text{g})$  is estimated from the overall average of the 298 K value and the average of the 200 K and 100 K data,[1]  $C_p(\text{Cl}_2, \text{g})$  is estimated as the average of the 298 K and 200 K values.[1]  $\text{Cl}_2(\text{l})$  boils at 239 K at 1 atm. with  $\Delta_{\text{vap}}H(\text{Cl}_2, \text{l})/(\text{kJ mol}^{-1}) = 20.41$ .[4]  $C_p(\text{Cl}_2, \text{l})$  is not known, so that the edge  $l$  cannot be fully evaluated.

$$\begin{aligned}
m/(\text{kJ mol}^{-1}) &= [C_p(\text{Na}^+, \text{g}) + C_p(\text{Cl}^-, \text{g}) + \frac{1}{2} C_p(\text{H}_2, \text{g})] \Delta T'''' \\
&\approx [20.8 + 20.8 + \frac{1}{2} \times \frac{1}{2} (28.8 + \frac{1}{2} \{27.4 + 28.2\})] (298 - 170) / 1000 \\
&= (55.75)(128) / 1000 = 7.1 \tag{S14}
\end{aligned}$$

$C_p(\text{H}_2, \text{g})$  is estimated from the overall average of the 298K value and the average of the 200K and 100K data.[1]

$$\begin{aligned}
n/(\text{kJ mol}^{-1}) &= [C_p(\text{NaCl}, \text{s}) + \frac{1}{2} C_p(\text{H}_2, \text{g})] \Delta T'''' \\
&\approx [50.50 + \frac{1}{2} \times \frac{1}{2} (28.8 + \frac{1}{2} \{27.4 + 28.1\})] (298-170) / 1000 \\
&\approx [50.50 + 14.15] (128) / 1000 = 8.3 \tag{S15}
\end{aligned}$$

$C_p(\text{H}_2, \text{g})$  is estimated from the overall average of the 298 K value and the average of the 200 K and 100 K data[1] and, in the absence of a value at 170 K, the 298 K value is taken for  $C_p(\text{NaCl}, \text{s})$ .

$$o/(\text{kJ mol}^{-1}) = \Delta_f H_{170\text{ K}}(\text{HCl}, \text{l}) \quad (\text{S16})$$

$$p/(\text{kJ mol}^{-1}) = [\Delta_f H_{170\text{ K}}(\text{Na}^+, \text{g}) + \Delta_f H_{170\text{ K}}(\text{Cl}^-, \text{g})] \quad (\text{S17})$$

Neither of the edges  $o$  and  $p$  can be quantified using existing literature. However, rough estimates may be made from a Born-Haber-Fajans cycle and the following phase change data:

$$\Delta_f H(\text{HCl}, \text{g})/(\text{kJ mol}^{-1}) \cong -92.2 \text{ at } 170\text{K} [1]$$

$$\Delta_{\text{vap}} H(\text{Cl}_2, \text{l})/(\text{kJ mol}^{-1}) = 20.41 [4]$$

$$\Delta_{\text{vap}} H(\text{HCl}, \text{l})/(\text{kJ mol}^{-1}) = 16.9 \quad (\text{S12})$$

$$\text{Thus: } o/(\text{kJ mol}^{-1}) = -88 \quad \text{and} \quad l/(\text{kJ mol}^{-1}) = 3.0 \quad (\text{S18})$$

$$q/(\text{kJ mol}^{-1}) = [U_{\text{POT}}(\text{NaCl}) - RT] = 786 - 1.45 = 785 \quad (\text{S19})$$

### Subsidiary Data

$$\Delta_f H_{350\text{ K}}(\text{NaCl}, \text{s})/(\text{kJ mol}^{-1}) = -412.4 [5] \quad (\text{S20})$$

$$\Delta_f H_{350\text{ K}}(\text{HCl}, \text{g})/(\text{kJ mol}^{-1}) = -92.3 [5] \quad (\text{S21})$$

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